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Characterizing Hydrogen Storage Media: Understanding the Interior Pore Structure of a Cu_3BTC_2 Metal-Organic Framework Infiltrated with $NaAlH_4$

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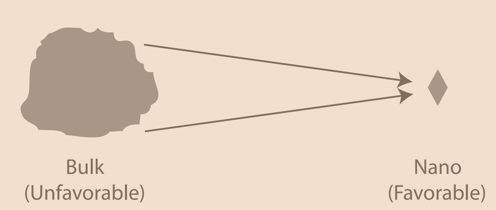
General Interest in Metal Hydrides and Metal-Organic Frameworks (MOFs)

Recent theoretical studies suggest that decreasing the bulk dimensions of metal hydrides to the nanometer scale produces thermodynamically favorable conditions for efficient hydrogen adsorption and desorption as opposed to the less favorable properties of the bulk material.[1]



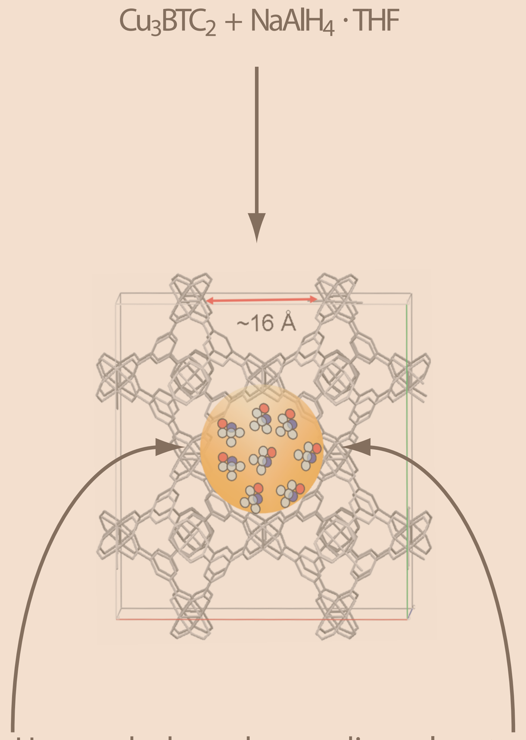
Why Use Metal-Organic Frameworks?

MOFs serve as the ideal medium for validating the theory relating sodium alanate particle size to molecular hydrogen storage properties.

The copper benzene tricarboxylate (CuBTC) framework is appealing due to its resistence to the chemically-reactive sodium alanate, allowing the MOF to function as an appropriate hydrogen storage material after infiltration with the metal hydride[2] without suffering from chemical breakdown.

Cu_3BTC_2 Infiltration with Sodium Alanate

$Cu_3BTC_2 + NaAlH_4 \cdot THF$



How and where does sodium alanate occupy the interior of the MOF?

Interior pore diameter suggests the likelihood of occupation by sodium alanate conglomerates upon infiltration with THF, and previous studies[2] support the formation of nanometer-scale sodium alanate conglomerates.

Why not "typical" porous media?

Ubiquitous porous media, such as zeolites, can vary in pore opening and interior dimensions over the macroscopic scale--inferring varied size distributions for particles within the pores, making it difficult to relate particle size to functionality.

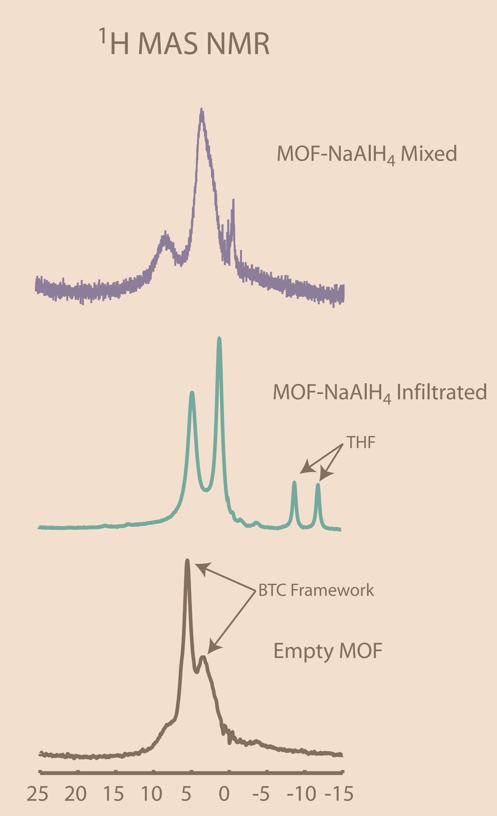
CuBTC MOF pores are consistent in both size and spacing, dependent on the specific MOF backbone. MOFs also posess long-range order over the macroscopic scale as opposed to similar materials such as zeolites; yielding consistent distribution of particle size throughout the matrix for infiltrated molecues, thus making MOFs an ideal host material for verifying pore confinement and nanoscale properties of metal hydrides, in addition to functioning as a hydrogen storage medium.

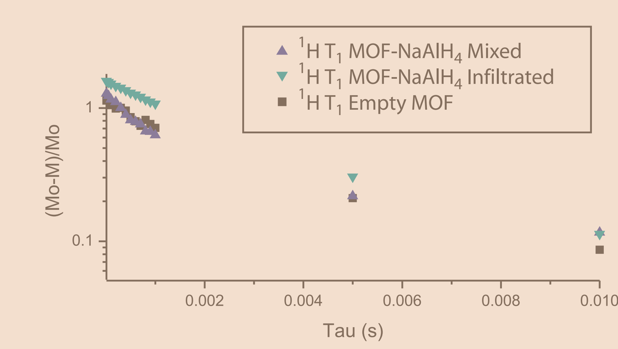
MOFs also offer an unparalleled amount of chemical variation for tailor-making a particular matrix with specific dimensions[3] for a particular applications such as size-exclusion or preferential-binding

Theory also indicates[4] that the more favorable thermodynamic conditions for hydrogenation and dehydrogenation by sodium alanate at the nanoscale within an organic framework is due to a charge-transfer interruption between Na+ and AlH4- by the electronegative carbon support framework of materials like MOFs.

Sodium Alanate and Pore Confinement

Proton NMR--Sodium Alanate Infiltrated vs. Mixed with Cu_3BTC_2



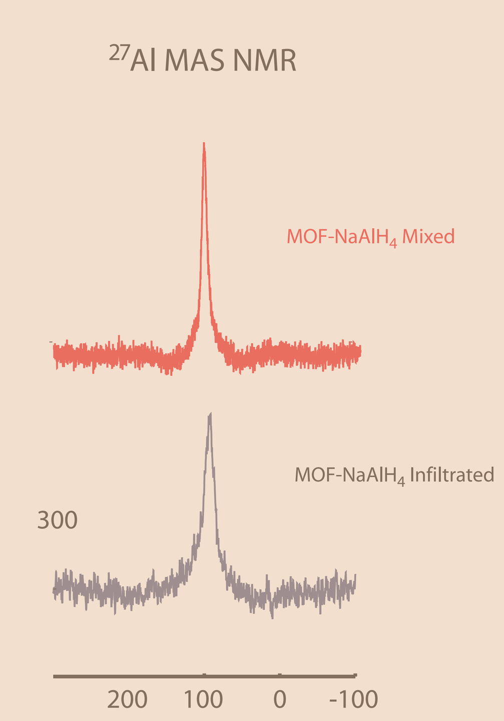


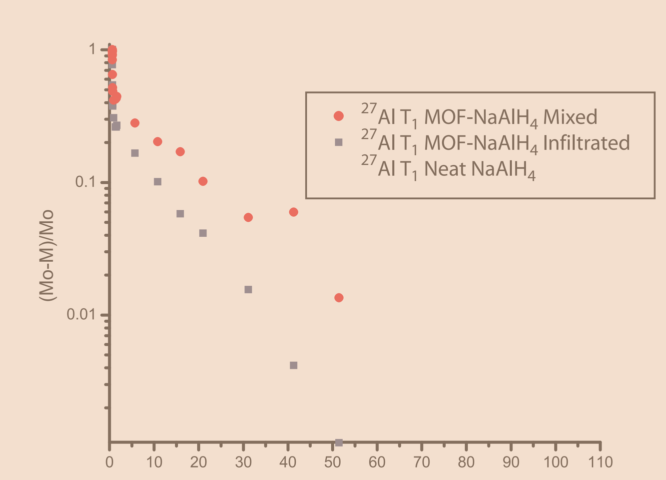
Infiltrated MOF proton NMR spectra show the retention of THF even after prolonged heating and evacuation.

Proton T_1 relaxation times appear relatively featureless to indicate the possible sodium alanate environment taken on within the MOF pore structure

-Further investigation of T_1 relaxation on residual THF in the infiltrated sample shows a more rapid relaxation rate of the THF protons in comparison to pure THF, indicating close proximity to the paramagnetic Cu^{2+} on the CuBTC paddlewheel units

Aluminum NMR--Sodium Alanate Infiltrated vs. Mixed with Cu_3BTC_2



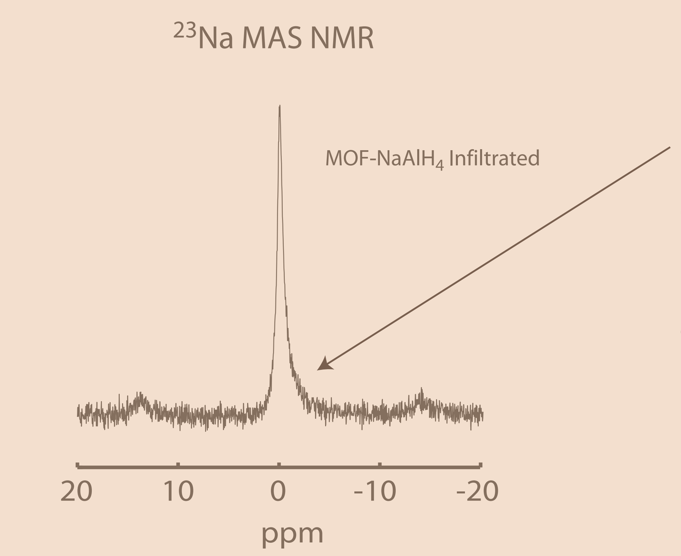


While spectrally similar, ^{27}Al resonances of sodium alanate mechanicaly mixed with the MOF vs. infiltrated via THF have distinctly different T_1 relaxation times. Additionally, the relaxation times of the mixed vs. neat NaAlH4 are nearly identical, indicating bulk properties of sodium alanate with the MOF unless infiltrated via THF.

The shorter ^{27}Al T_1 relaxation time of the infiltrated sample vs. that of mixed and neat sodium alanate indicates close proximity of the sodium alanate to the paramagnetic Cu^{2+}, likely occupying the tetrahedral holes around the CuBTC paddlewheel units.

Interpreting Local Adsorption Environment

Sodium NMR and Lineshape Analysis



Asymmetric lineshape in the ^{23}Na MAS NMR spectra for sodium alanate infiltrated into the CuBTC MOF matrix indicates a non-isotropic local electric field gradient.

$$P_Q = \frac{1}{\sqrt{2\pi\sigma^5}} \nu_Q^4 \eta \left(1-\frac{\eta^2}{9}\right) exp\left[-\frac{\nu_Q^2\left(1+\frac{\eta^2}{3}\right)}{2\sigma^2}\right]$$

The Czjzek model[5] for quadrupolar nuclei in ordered solids may be applied and can provide local electric field gradient information of the sodium alanate infiltrated into the MOF matrix, further supporting the location--and perhaps the size distribution--of sodium alanate conglomerates within the MOF matrix.

Conclusions

-Preliminary results support the nano-confinement of sodium alanate within the pores of a Cu_3BTC_2 MOF substrate.

-Increased ^1H and ^{27}Al NMR T_1 relaxation rates indicate a close proximity of infiltrated sodium alante to the paramagnetic Cu^{2+} ions on the BTC paddlewheel units. This is in support of the theory that an interaction due to the electronegative framework with the sodium alanate facilitates thermodynamically-favorable hydrogen adsorption and desorption.

-Further studies can elucidate the local electronic environment of the sodium ions, further supporting a charge-transfer mechanism as the driving force for thermodynamically-favorable hydrogen adsorption and desorption.

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